

## COMPOSITION FOR PROTECTION OF GLASSWARE IN DISHWASHERS

The present invention relates to a composition comprising zinc and bismuth for use in the protection of glassware in an automatic dishwasher process particularly from detrimental phenomena caused by the presence of aluminium.

The problem of glassware corrosion in automatic dishwasher processes is well recognised. It has been put forward that the problem of glassware corrosion is the result of two separate phenomena. Firstly, it is suggested that the corrosion is due to leakage of minerals from the glass network, accompanied by hydrolysis of the silicate network. Secondly, silicate material is suggested to be released from the glass.

These phenomena can cause damage to glassware after a number of separate wash cycles. The damage may include cloudiness, scratches, streaks and other discoloration / detrimental effects.

Silicate materials have been suggested to be effective in preventing materials from being released by the glass composition. However, the use of silicate compounds can have detrimental side effects, such as the tendency to increase separation of silicate material at the glass surface.

A further solution has been to use zinc, either in metallic form (such as described in US Patent No. 3,677,820) or in the form of compounds. The use of soluble zinc compounds in the prevention of glassware corrosion in a dishwasher is described in, for example, US Patent No. 3,255,117.

The use of glasses and ceramics containing zinc has been found to address the problem of glassware corrosion in a dishwasher. WO-A-01/64823 describes the use of a ceramic composition comprising zinc to protect glassware in an automatic dishwashing process. GB-A-2 372 500 and WO-A-00/39259 describe the use of a soluble glass composition comprising zinc (present in the form of ions) to protect glassware in an automatic dishwashing process. The use of a ceramic / glass zinc containing composition overcomes the problems of poor solubility / precipitation described above whilst offering effective glassware protection.

However, there is still a problem associated with the ceramic / glass zinc containing compositions (and also with water soluble / insoluble zinc compounds) in that these compositions do not perform satisfactorily in the prevention of decorated glassware corrosion.

Bismuth has been used as an additive to aid the prevention of corrosion of glazed glassware corrosion. For example, BE 860180 describes the use of bismuth to avoid damage of decorated, glazed articles. However, the value of bismuth in this purpose has been diminished by the detrimental effects that the use of bismuth compound has on other components of the washing process. In this regard bismuth has been found to stain plastic materials (such as Tupperware®). Bismuth also causes the formation of a brown stain on non-decorated glassware and cutlery. Also although the glazed portion of the glassware may receive protection, bismuth has been found to stain the non-glazed portions. For these reasons the use of bismuth as a glaze protector has been avoided.

A further problem which may be encountered when washing glassware in a dishwasher, and which has as yet not been addressed by automatic dishwasher detergent manufactures, is that caused by the presence of aluminium ions in the dishwasher.

In the past aluminium has been put forward as a glass corrosion inhibition agent in, for example, US Patent No. 3,255,117 and WO-A-96/36687, for fine tableware such as lead crystal.

However, there is some doubt that aluminium is entirely effective in this aim: whilst a reduction in mass loss and cord lines, when the glass is washed repeatedly in an automatic dishwasher is observed, glass clouding is exacerbated.

Additionally, a major problem with the use of aluminium is that, with use, the glassware adopts an iridescence. This has the effect of changing the glass from being transparent and colourless to having a coloured hue. Indeed, it has been observed that the detrimental efficacy of aluminium in this regard is so high that even when aluminium is present in a very small amount in the dishwasher liquor this effect is observed. As an example, the use of aluminium based dyes in dishwasher detergents, even in the minuscule quantities that such dyes are required, is avoided so that the iridescence effect does not occur.

Clearly this detrimental effect on glassware is undesirable. As a result the presence of aluminium in automatic dishwashing detergents has had to be avoided. However, although the aluminium content of a detergent (and also the automatic dishwashing machine) can be controlled

and is usually kept as low as possible, the action of a consumer can still lead to exposure of glassware to aluminium. This can happen if, for example, a user washes an aluminium item (such as a common household garlic press) in an automatic dishwasher. In this instance the release of aluminium into the dishwasher liquor is enough to cause the detrimental effects described above. This effect may even be apparent after the single wash cycle the effect has also been observed if the user washes other aluminium items such as some pre-prepared food containers in the dishwasher. The effect may also be caused if the dishwasher contains any exposed aluminium components such as screws or sieves.

The problem of metallic aluminium dissolution leading to the iridescent issues is particularly pronounced in a dishwashing machine as the dishwasher liquor is normally alkaline and aluminium dissolution enhanced at high pH.

A further detrimental effect associated with the use of aluminium is that aluminium is known to exacerbate glass clouding corrosion. This is in contrast to the positive effect of aluminium on mass loss and cord lines. Clearly this detrimental effect prevails over any positive effect and is to be avoided.

It is an object of the present invention to obviate / mitigate the problems outlined above.

According to a first aspect of the present invention there is provided the use of a composition comprising zinc and bismuth for the protection of glassware in an automatic dishwashing process from detrimental effects caused by exposure of the glassware to aluminium.

It will be appreciated that the composition is for use in addressing potential problems which may be caused by exposure of glassware to a source of aluminium in a dishwasher liquor.

In the present invention it is understood that the term glassware includes items made of glass (such as drinking glasses and plates) which may be decorated (such as with a glaze and / or with etching / glass addition). The term glassware is also understood to include other items of houseware, which may comprise a material other than glass (such as a ceramic) but which have a glass / glaze coating or decoration (such as a glazed ceramic plate).

It has been found that a combination of zinc and bismuth has especially beneficial properties in the prevention of detrimental effects (such as iridescence) caused by the presence of aluminium in the dishwasher liquor in an automatic dishwashing process. Additionally the use of the composition is highly effective at protecting normal glassware and also the composition has been found to be highly effective in protecting glazed glassware / crockery. Thus a single composition may now be used to provide glassware corrosion protection for both decorated glassware / crockery and non-decorated glassware in a dishwasher, as well as tackling the issues raised by the presence of aluminium.

The ratio of zinc to bismuth in the composition used is preferably in the range from 1:100 to 100:1 (based on mass of the metals). More preferably the ratio of zinc to bismuth in the composition (by mass) is from 1:10 to 10:1,

more preferably from 1:5 to 5:1 and most preferably about 1:1.

Bearing the ratios outlined above in mind, the amount of zinc and bismuth provided to a dishwasher cycle is preferably from 1 to 1000 mg, more preferably from 1 to 500mg, more preferably from 1 to 200mg and more preferably 5 to 100mg. Preferably this weight refers to the combined weight of both metals.

Most preferably the zinc and bismuth are available as ions in the dishwasher washing liquor.

The zinc and bismuth may be in any suitable form to provide ions in the dishwasher liquid.

One example of a suitable form is the use of a metallic form of the metals. This form may be as separate forms of each metal disposed within the dishwasher. Such forms have been found to be solubilised over a number of wash cycles, to provide soluble ions of bismuth and zinc. The metal form may also comprise an admixture (such as an alloy) of zinc and bismuth. The alloy may contain further elements, such as other metal elements necessary to ensure stability / solubility of the alloy.

Preferred physical forms of the metal / alloy include sheets, perforated sheets, fibres, granules, powders, blocks (e.g. cuboid) or an admixture thereof.

Another example of a suitable form is the use of a salt or compound of one or both of bismuth and zinc. Most preferably the salt / compound is one which has an appreciable solubility in the washing liquor so that the

effect of the zinc and bismuth can be observed. However, a salt of either element which only has a low solubility may also be used. In the latter case (as when a metallic form of one or more of the elements themselves is used) the amount of salt / compound which is used in the dishwasher may be increased accordingly to counter the low solubility of the low solubility salts.

Most preferably the salt / compound does not contain a component which is aggressive / detrimental to the dishwasher/ dishwasher contents. In the case where the salt / compound is ionic it is preferred that the salt / compound is free from chloride anions which are recognised to have a detrimental effect on dishwashers (more particularly on stainless steel dishwasher components / cutlery).

Preferred examples of soluble metal salts include compounds with anions such as nitrate, sulphate, halide (especially fluoride), phosphate (where soluble), carbonate and carboxylate (such as the anions from C<sub>1</sub>-C<sub>10</sub> mono or multi carboxy function containing carboxylic acids, especially acetate and citrate).

Preferred examples of metal compounds having a lower solubility include the oxides of the metals.

An admixture of more than one compound may be used. Also a different compound of each metal may be used.

Most preferably the salt / compound is part of a detergent formulation. The detergent formulation may comprise a rinse aid.

The detergent formulation may be any common detergent formulation of the type which are usually employed with dishwashers. The formulation may comprise a liquid, gel, powder or tablet formulation. Where the formulation is a liquid / gel generally the zinc and bismuth will be present in solution within the liquid / gel. However, it is also contemplated to have the zinc and bismuth present in the liquid /gel in the form of an insoluble salt /compound so that the zinc / bismuth may comprise a suspended particle (e.g. such as a "speckle" typically found in these formulations).

The detergent formulation normally comprises other components which are typically found in dishwasher detergent formulations. In this regard the detergent formulation typically comprises one or more components selected from the group comprising surfactants (non-ionic, anionic, cationic and zwitterionic), builders, enzymes, foam suppressants, bleaches, bleach activators, thickeners, perfumes and dyes.

It is most preferred that when the bismuth and zinc are present together in a dishwasher detergent formulation, the metals comprise from 0.002 to 6wt% (based on the weight of both metals) of the detergent formulation. More preferably the metals comprise from 0.01 to 3wt% and most preferably from 0.02 to 1.3wt% of the dishwasher detergent formulation (e.g. 0.4wt% for a 20 g tablet).

In the case of a rinse aid, especially when the rinse aid is the only source of bismuth and zinc for the dishwasher, it is preferred that the metals comprise from 0.03 to 30wt% (based on the weight of both metals) of the rinse aid formulation. More preferably the metals comprise from 0.15



to 15wt% and most preferably from 0.3 to 7wt% of the rinse aid formulation.

The zinc and / or bismuth may also be present in a soluble ceramic / glass formulation. The glass / ceramic may contain a glass forming material such as silica ( $\text{SiO}_2$ ) or a boron oxide (e.g.  $\text{B}_2\text{O}_3$ ), an alkali / alkaline metal oxide (e.g.  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ) and /or a phosphorus oxide (e.g.  $\text{P}_2\text{O}_5$ ).

The glass / ceramic may comprise a homogenous body or in the alternative may be ground / crushed. Where the glass / ceramic is ground or crushed it preferably has an average particle size of less than 500 $\mu\text{m}$ .

It will also be appreciated that for all the forms of the bismuth and zinc mentioned above an admixture of different forms, wherein each metal is present in a different physical format may be used.

In this regard it is also possible that one of the metals may be present in an additive whilst the other metal may be present in a detergent / rinse-aid formulation. As an example the zinc may be present in the dishwasher detergent / rinse-aid together with one or more other detergent components whilst the bismuth may be added as a separate additive such as a glass composition which is disposed within the dishwasher machine. Clearly other combinations of physical forms which satisfy the requirement that both bismuth and zinc are supplied to the wash liquor in accordance with the present invention.

Strangely it has also been found that when a combination of bismuth and zinc has been used to address the problems caused by the presence of aluminium in the dishwasher

liquor not only have the detrimental effects caused by the aluminium being eliminated but furthermore the positive effects of the bismuth and zinc on the prevention of decorated and non-decorated glassware corrosion have been enhanced.

Thus in accordance with the second aspect of the invention there is provided a composition comprising zinc, bismuth and aluminium for the protection of the glassware in an automatic dishwasher.

Surprisingly when this composition is used in an automatic dishwasher over repeated wash cycles the previously observed detrimental effect of glass clouding attributed to the presence of aluminium is vastly reduced.

It will be appreciated that features of the first aspect of the invention shall apply *mutatis mutandis* to the second aspect of the invention.

The aluminium may be present in the composition in any form (e.g. metallic form, fully / partially soluble aluminium salt / organic compound). Preferably the aluminium is present in the formulation such that from 5 to 200mg of aluminium is released per wash cycle.

Additionally it has been found that when a combination of zinc and bismuth has been used to address the problems caused by the presence of aluminium ions in the dishwasher, this composition, if used in combination with a source of silicate, is able to achieve the same effects in terms of glass corrosion protection but also corrosion protection for aluminium items placed in the dishwasher (previously a widely observed problem) is greatly improved.

Thus in accordance with a third aspect of the invention there is provided a composition comprising zinc, bismuth and silicate for the protection of aluminium items in an automatic dishwasher.

Surprisingly when this composition is used in an automatic dishwasher over repeated wash cycles the previously observed detrimental occurrence of aluminium corrosion is vastly reduced.

It will be appreciated that features of the first aspect of the invention shall apply *mutatis mutandis* to the third aspect of the invention.

Preferably the amount of silicate is present in a ratio of up to 1000:1 based on the weight of the zinc and bismuth components (with the term weight referring to the weight of the elements *per se* in any compound / admixture containing same). More preferably the amount of silicate is present in a ratio to zinc and bismuth of up to 500:1 and most preferably up to 100:1.

The silicate may be present in the composition in any form (e.g. fully/partially soluble salt, organic compound (e.g. silicone), water soluble glass or ceramic).

The silicate preferably comprises an admixture of a metal oxide (e.g. an alkali metal oxide such as sodium  $\text{Na}_2\text{O}$  or potassium  $\text{K}_2\text{O}$ ) and silica ( $\text{SiO}_2$ ). The preferred ratio of silica to metal oxide is between 1.0 to 4.0. A preferred example of a silicate is a metal (e.g. an alkali metal) disilicate such as  $\text{Na}_2\text{Si}_2\text{O}_5$ , (metal oxide to silica ratio of 2.0).

The invention is now further described with reference to the following non-limiting Examples.

### Examples

#### Glassware Corrosion Examples

In the Examples the following detergent composition (as shown in Table GL 1a) was used as a detergent formulation base. The formulation was used in tablet form.

**Table GL 1a**

Component	%
Sodium Tripolyphosphate	45.0
Sodium Bicarbonate	2.0
Sodium Carbonate	18.5
Sodium Perborate	10.0
TAED	2.5
Protease	1.5
Amylase	0.5
Non-ionic Surfactant	3.5
Polyethylene-glycol)	7.5
Perfume + Dye	0.3
Auxiliaries	Rest

In the Examples the following glass composition was used as a source of zinc and bismuth (as shown in Table GL 1b). The glass formulation used was in the form of a solid body (measuring 4cm x 1cm x 1cm).

**Table GL 1b**

Component	%
P <sub>2</sub> O <sub>5</sub>	60.0
K <sub>2</sub> O	20.3
Bi <sub>2</sub> O <sub>3</sub>	3.2 (2.86% Bi)
B <sub>2</sub> O <sub>3</sub>	1.3
CaO	1.0
ZnO	14.2 (11.4% Zn)

When used in accordance with the method described below the mass loss of the glass block was on average 0.35 g/cycle, equating to 10mg Bi<sup>3+</sup> per cycle and 40mg Zn<sup>2+</sup> per cycle.

**Test Method**

In the Examples test glasses were washed 50 to 100 times in a special endurance test dishwasher (Miele G 541 Special).

Cleaning Dosage: A 20g tablet of the base detergent described above was used with alternative additives (as specified in the Examples). Automatic dosing of the tablet occurred at the beginning of the cleaning cycle.

Water Hardness in the machine: less than 0.5dGH, central softening through ion exchangers, internal ion exchangers not in operation.

Cleaning program 65°C (both the cleaning and the rinse cycle were operated at 65°C).

Water consumption per cycle: 23.5 litres.

There was no soiling of the glassware tested.

The test report comprised the following types of glass:

#### **Clear Glasses**

Luigi Bormoli (Italy):

"linea Michelangelo David" C32 Whitewine glass 19 cl.

Arc-International (France):

"Luminarc Octime Transparent", Whisky glass 30cl.

"Longchamp", 17cl, Stemglass, lead crystal glass.

"Arcoroc Elegance", Wineglass, 14,5 cl.

Ruhr Kristall Glas (Germany):

"Kölner Stange", 24cl, beer glass.

"RKG Bier", Beer Stemware, 38 cl.

Nachtmann Bleikristallwerke (Germany):

"Longdrink-glass", special edition (dishwasher sensitive),  
produced especially for Reckitt Benckiser.

#### **Decorated Glassware**

Ruhr Kristall Glas (Germany):

"Snoopy Look In", Longdrink Nordland 28 cl.

"Teddy", Primusbecher 16 cl.

Arc-International (France):

"Kenia", dinner plate, 19,5 cm.

The weight loss was determined gravimetrically after 50 to 100 test washes. Visible changes to the glass surface were evaluated in natural light (iridescence) or in a special light box (glass clouding, line corrosion and decoration

damage). The dimensions of the light box were 70cm x 40cm x 65cm (l x b x h) and the inside of the box was painted matt black. The box was lit from above with an L 20w/25S (60cm long) Osram lamp, which was covered in front with a screen. Shelves were disposed in the box on which the glasses were placed for evaluation. The box was open at the front.

The glass corrosion was evaluated using the following criteria; glass clouding (GC), line corrosion (CL), decoration damage (DS) and iridescence (IR). For each parameter a score was given in accordance with the table below.

Evaluation	Damage Impact
0	No glass damage
1	First minor damage / hardly visible
2	Slight damage, visible to expert or in the light box
3	Visible damage
4	Strong damage, clearly visible

#### Comparative Example 1

In this Comparative Example only the base detergent formulation was used.

The results of the tests are shown in Table GL 2a (Glass Corrosion) and Table GL 2b (Mass Loss).

**Table GL 2a - Glass Corrosion**

<b>Glasses</b>	<b>50 cycles</b>			<b>100 Cycles</b>		
	<b>GC</b>	<b>CL</b>	<b>IR</b>	<b>GC</b>	<b>CL</b>	<b>IR</b>
Michelangelo	2.5	3.0	0.0	2.5	4.0	0.0
Octime	1.0	3.0	0.0	2.0	4.0	0.0
Longchamp	3.5	3.0	0.0	4.0	4.0	0.0
RKG Kölsch	0.5	3.0	0.0	1.0	4.0	0.0
RKG Bier	2.5	3.5	0.0	3.0	4.0	0.0
Nachtmann Longdrink	3.0	0.0	0.0	4.0	0.0	0.0
Arcoroc Elegance	3.0	3.5	0.0	4.0	4.0	0.0
<i>Average</i>	<i>2.29</i>	<i>2.71</i>	<i>0.0</i>	<i>2.93</i>	<i>3.43</i>	<i>0.0</i>
<b>Decorated Glassware</b>	<b>DS</b>	<b>IR</b>	<b>DS</b>	<b><u>IR</u></b>		
Snoopy	3.0	-	3.5	-		
Teddy	3.5	-	4.0	-		
Kenia Plates	3.5	0.0	4.0	0.0		
<i>Average</i>	<i>3.33</i>	<i>-</i>	<i>3.83</i>	<i>-</i>		



**Table GL 2b - Mass Loss**

<b>Glasses</b>	<b>50 cycles Mass Loss (mg)</b>	<b>100 cycles Mass Loss (mg)</b>
Michelangelo	35	59
Octime	25	48
Longchamp	58	94
RKG Kölsch	24.5	45.5
RKG Bier	40	72
Nachtmann Longdrink	70	124
Arcoroc Elegance	17	30
<i>Sum</i>	<i>269.5</i>	<i>472.5</i>
<b>Decorated Glassware</b>		
Snoopy	223	502
Teddy	67	145
Kenia Plates	110	230
<i>Sum</i>	<i>400</i>	<i>877</i>

**Comparative Example 2**

In this Comparative Example only the base detergent formulation was used. In addition an aluminium garlic press was present in the dishwasher.

The results of the tests are shown in Table GL 3a (Glass Corrosion) and Table GL 3b (Mass Loss).

Table GL 3a - Glass Corrosion

Glasses	50 cycles			100 Cycles		
	GC	CL	IR	GC	CL	IR
Michelangelo	2.5	1.5	2.5	4.0	4.0	3.0
Octime	2.5	2.0	2.0	3.0	3.5	2.5
Longchamp	1.5	2.0	3.0	4.0	4.0	3.0
RKG Kölsch	1.5	1.0	2.0	3.5	3.0	2.5
RKG Bier	3.0	2.0	2.5	4.0	4.0	3.0
Nachtmann Longdrink	3.5	0.0	3.0	4.0	0.0	3.5
Arcoroc Elegance	2.0	0.5	2.0	4.0	3.0	2.0
<i>Average</i>	<i>2.36</i>	<i>1.29</i>	<i>2.5</i>	<i>3.79</i>	<i>3.07</i>	<i>2.81</i>
<b>Decorated Glassware</b>	<b>DS</b>	<b>IR</b>	<b>DS</b>	<b><u>IR</u></b>		
Snoopy	2.5	-	3.5	-		
Teddy	2.5	-	3.5	-		
Kenia Plates	3.0	3.0	3.5	3.0		
<i>Average</i>	<i>2.67</i>	-	<i>3.5</i>	-		

Table GL 3b - Mass Loss

Glasses	50 cycles Mass Loss (mg)	100 cycles Mass Loss (mg)
Michelangelo	8	25
Octime	5.5	12.5
Longchamp	21	49
RKG Kölsch	6	13
RKG Bier	23	53
Nachtmann Longdrink	24	55
Arcoroc Elegance	7	14
Sum	94.5	221
<b>Decorated Glassware</b>		
Snoopy	77	181
Teddy	16	46
Kenia Plates	35	93
Sum	128	320

Comparative Examples 1 and 2 show that whilst aluminium is able to provide mass loss / line corrosion protection for both decorated and non-decorated glassware it causes an iridescence effect on both decorated and non-decorated glassware (when present in the dishwasher liquor in metallic form as a garlic press). Aluminium also exacerbates glass clouding corrosion - this is particularly noticeable after 100 wash cycles.

**Example 1**

In this Example the bismuth and zinc containing glass was used in addition to the base detergent tablet.

The aluminium garlic press was also present in the dishwasher.

The results are shown in Table GL 4 (Iridescence).

**Table GL 4 - Iridescence**

<b>Glasses</b>	<b>50 cycles</b>	<b>100 Cycles</b>
	<b>IR</b>	<b>IR</b>
Michelangelo	0.0	0.0
Octime	0.0	0.0
Longchamp	0.0	0.0
RKG Kölsch	0.0	0.0
RKG Bier	0.0	0.0
Nachtmann Longdrink	0.0	0.0
Arcoroc Elegance	0.0	0.0
<i>Average</i>	<i>0.0</i>	<i>0.0</i>
<b>Decorated Glassware</b>	<b>IR</b>	<b><u>IR</u></b>
Snoopy	-	-
Teddy	-	-
Kenia Plates	0.0	0.0
<i>Average</i>	-	-

The results of Example 1 show that the presence of both bismuth and zinc completely eliminates the detrimental effect of iridescence caused by the presence of the aluminium.

**Example 2**

In this Example the bismuth and zinc containing glass was used in addition to the base detergent tablet.

The aluminium garlic press was also present in the dishwasher (however, please see next paragraph).

The results of the tests are shown in Table GL 5a (Glass Corrosion) and Table GL 5b (Mass Loss). In these tables the figures shown in parentheses were achieved in the absence of aluminium - namely with only the detergent formulation and the bismuth and zinc water soluble glass block. The remaining figures show the results achieved in the presence of the aluminium garlic press.

Table GL 5a - Glass Corrosion

Glasses	50 cycles		100 Cycles	
	GC	CL	GC	CL
Michelangelo	0.5(1.5)	1.0 (1.5)	2.5(2.0)	1.5(3.0)
Octime	2.0(2.5)	1.0 (1.0)	2.5(2.5)	1.5(2.5)
Longchamp	0.0(1.0)	0.5(1.0)	0.5(2.5)	1.0(3.0)
RKG Kölsch	0.0(0.0)	1.0 (1.0)	0.0(1.0)	2.0(2.0)
RKG Bier	1.5(1.5)	1.0 (0.5)	2.0(2.0)	1.0(2.0)
Nachtmann Longdrink	2.0(2.5)	0.0(0.0)	4.0(4.0)	0.0(0.0)
Arcoroc Elegance	1.5(2.0)	1.0 (1.5)	2.5(3.5)	2.0(2.5)
<i>Average</i>	<i>1.07</i> <i>(1.57)</i>	<i>0.79</i> <i>(0.93)</i>	<i>2.0</i> <i>(2.50)</i>	<i>1.29</i> <i>(2.14)</i>
<b>Decorated Glassware</b>	<b>DS</b>		<b>DS</b>	
Snoopy	1.0(1.5)		2.0(2.5)	
Teddy	1.5(2.0)		2.5(2.5)	
Kenia Plates	1.0(2.0)		2.0(3.0)	
<i>Average</i>	<i>1.17(1.83)</i>		<i>2.17(2.67)</i>	

**Table GL 5b - Mass Loss**

<b>Glasses</b>	<b>50 cycles Mass Loss (mg)</b>	<b>100 cycles Mass Loss (mg)</b>
Michelangelo	3.0(11)	(25)
Octime	0.0(14.5)	(20.5)
Longchamp	3.0(19)	(30)
RKG Kölsch	2.0(9.5)	(18.5)
RKG Bier	5.0(13)	(26)
Nachtmann Longdrink	0.0(26)	(34)
Arcoroc Elegance	2.0(9)	(14)
<i>Sum</i>	<i>15.0(102)</i>	<i>(168)</i>
<b>Decorated Glassware</b>		
Snoopy	7.0(62)	21.0(121)
Teddy	6.0(24)	13.0(46)
Kenia Plates	20.0(33)	31.0(61)
<i>Sum</i>	<i>33.0(119)</i>	<i>65.0(228)</i>

Example 2 surprisingly shows that a formulation containing a combination of zinc and bismuth, when combined with a source of aluminium (the garlic press) provides enhanced glassware corrosion protection (when compared to a combination of zinc and bismuth).

Additionally the enhanced glassware corrosion protection is achieved without observation of any of the detrimental effects that would normally be caused by the presence of aluminium. Namely both iridescence caused by the presence of aluminium and excessive glass clouding are not observed.

These effects are both unexpected.

Furthermore the composition offers protection for both non-decorated and decorated glassware.

#### Aluminium Corrosion Examples

In the Examples the following detergent composition (as shown in Table AL1a) was used as a detergent formulation base. The formulation was used in tablet form.

**Table AL1a**

Component	%
Sodium Tripolyphosphate	45.0
Sodium Bicarbonate	2.0
Sodium Carbonate	18.5
Sodium Perborate	10.0
TAED	2.5
Protease	1.5
Amylase	0.5
Non-ionic Surfactant	3.5
Polyethylene-glycol)	7.5
Perfume + Dye	0.3
Auxiliaries	Rest



**Test Method**

In the Aluminium Examples the test methods used were as those used in the Glass Examples.

**Clear Glasses**

The glasses used (decorated and non-decorated) were as those used in the Glass Examples. The evaluation of the glass corrosion was carried out in the same manner as for the Glass Examples.

**Aluminium Plates**

Two aluminium plates were added to the dishwasher. The plates comprised an alloy of magnesium and aluminium as (ALMg4 96% aluminium and 4% magnesium). The plates measured 100mm x 50 mm X 1.5mm and weighed 20g.

The weight loss was determined gravimetrically after 50 to 100 test washes.

The aluminium corrosion was evaluated using the following criteria; discoloration aluminium (DA) and Shine Units (SU). For DA a score was given in accordance with the table below.

<b>Evaluation</b>	<b>Damage Impact</b>
0	No aluminium damage
1	First minor damage / hardly visible
2	Slight damage, visible to expert
3	Visible damage
4	Strong damage, clearly visible

For SU the measurement technique according to the "Colour Guide Gloss" for handheld instruments from the company BYK Gardner GmbH was used. With the D65/10° setting and the measurement aperture set at 11mm, ten evaluations on the back and ten on the front side of the plate were performed. The measurement from these twenty evaluations was averaged.

#### Comparative Example 1

In this Comparative Example only the base detergent formulation was used.

The results of the tests are shown in Table AL2a (Glass Corrosion) and Table AL2b (Mass Loss).

**Table AL2a - Glass Corrosion**

Glasses	50 cycles			100 Cycles		
	GC	CL	IR	GC	CL	IR
Michelangelo	1.5	1.5	3.0	3.0	4.0	3.5
Octime	2.5	1.5	1.5	2.5	1.5	1.5
Longchamp	1.5	1.5	2.5	3.5	2.5	4.0
RKG Kölsch	0.5	1.5	2.0	2.0	2.0	2.0
RKG Bier	1.0	1.0	1.5	2.0	1.5	3.0
Nachtmann Longdrink	3.0	0.0	2.0	4.0	0.0	3.0
Arcoroc Elegance	1.0	0.5	1.0	3.5	2.0	1.5
Average	1.57	1.07	2.06	2.93	1.93	2.75
Decorated Glassware	DS		IR	DS		<u>IR</u>
Snoopy	2.0		-	3.0		-
Teddy	1.5		-	2.5		-
Kenia Plates	2.0		3.0	2.5		3.5
Average	3.33		-	2.67		-
Al-Plates	DA			DA		SU
Plate	1.0			1.5		4.1

**Table AL2b - Mass Loss**

<b>Glasses</b>	<b>50 cycles Mass Loss (mg)</b>	<b>100 cycles Mass Loss (mg)</b>
Michelangelo	7	59
Octime	9	48
Longchamp	15	94
RKG Kölsch	7	45.5
RKG Bier	6	72
Nachtmann Longdrink	15	124
Arcoroc Elegance	7	30
<i>Sum</i>	<i>66</i>	<i>472.5</i>
<b>Decorated Glassware</b>		
Snoopy	25	502
Teddy	12	145
Kenia Plates	20	230
<i>Sum</i>	<i>57</i>	<i>877</i>
<b>Al-Plates</b>		
Plate	2138	4698

**Comparative Example 2**

In this Comparative Example only the base detergent formulation was used. In addition 3.67g of sodium disilicate was added to the tablet formulation.

The results of the tests are shown in Table AL3a (Glass Corrosion) and Table AL3b (Mass Loss).

Table AL3a - Glass Corrosion

Glasses	50 cycles			100 Cycles		
	GC	CL	IR	GC	CL	IR
Michelangelo	2.0	3.5	3.5	2.5	4.0	4.0
Octime	2.5	3.0	3.0	3.5	4.0	3.5
Longchamp	4.0	3.5	3.5	4.0	4.0	4.0
RKG Kölsch	4.0	3.0	4.0	4.5	4.0	4.0
Nachtmann Longdrink	4.0	0.0	3.5	4.0	0.0	4.0
Arcoroc Elegance	4.0	4.0	3.5	4.0	4.0	4.0
Average	3.42	2.83	3.42	3.67	3.33	3.92
Decorated Glassware	DS		IR	DS		<u>IR</u>
Snoopy	3.0		-	3.5		-
Teddy	3.0		-	3.5		-
Kenia Plates	1.5		4.0	2.0		4.0
Average	2.5		-	3.0		-
Al-Plates	DA			DA		SU
Plate	3.5			4.0		34.9

**Table AL3b - Mass Loss**

<b>Glasses</b>	<b>50 cycles Mass Loss (mg)</b>	<b>100 cycles Mass Loss (mg)</b>
Michelangelo	29	52
Octime	15	22
Longchamp	76	109
RKG Kölsch	15	27
Nachtmann Longdrink	46	90
Arcoroc Elegance	10	23
<i>Sum</i>	<i>192</i>	<i>323</i>
<b>Decorated Glassware</b>		
Snoopy	130	256
Teddy	48	99
Kenia Plates	45	76
<i>Sum</i>	<i>223</i>	<i>431</i>
<b>Al-Plates</b>		
Plate	0.0	0.0

**Comparative Example 3**

In this Comparative Example only the base detergent formulation was used. In addition 0.67g of zinc acetate was added to the tablet formulation

The results of the tests are shown in Table AL4a (Glass Corrosion) and Table AL4b (Mass Loss).

**Table AL4a - Glass Corrosion**

Glasses	50 cycles			100 Cycles		
	GC	CL	IR	GC	CL	IR
Michelangelo	0.5	1.5	0.5	0.5	1.5	0.5
Octime	1.5	1.0	0.5	2.5	1.5	0.5
Longchamp	0.0	1.0	0.0	0.0	1.5	0.0
RKG Kölsch	0.5	2.0	0.5	1.5	2.5	1.0
Nachtmann Longdrink	0.5	0.0	1.0	0.5	0.0	0.5
Arcoroc Elegance	1.0	0.5	1.0	1.5	1.0	1.0
Average	0.67	1.00	0.58	1.08	1.33	0.58
Decorated Glassware	DS			DS		
Snoopy	1.0			2.0		
Teddy	1.0			1.5		
Kenia Plates	1.0			2.5		
Average	1.00			2.00		
Al-Plates	DA			DA		SU
Plate	2.0			3.0		73.2

**Table AL4b - Mass Loss**

<b>Glasses</b>	<b>50 cycles Mass Loss (mg)</b>	<b>100 cycles Mass Loss (mg)</b>
Michelangelo	15	16
Octime	2	0
Longchamp	7	17
RKG Kölsch	0	0
Nachtmann Longdrink	1	8
Arcoroc Elegance	1	7
<i>Sum</i>	<i>26</i>	<i>48</i>
<b>Decorated Glassware</b>		
Snoopy	14	32
Teddy	5	16
Kenia Plates	17	41
<i>Sum</i>	<i>36</i>	<i>89</i>
<b>Al-Plates</b>		
Plate	118	233

**Comparative Example 4**

In this Comparative Example only the base detergent formulation was used. In addition 0.19g of bismuth citrate was added to the tablet formulation.

The results of the tests are shown in Table AL5a (Glass Corrosion) and Table AL5b (Mass Loss).



**Table AL5a - Glass Corrosion**

Glasses	50 cycles			100 Cycles		
	GC	CL	IR	GC	CL	IR
Michelangelo	0.5	1.5	1.0	2.0	1.5	1.0
Octime	2.0	1.5	0.5	2.0	2.0	0.5
Longchamp	1.0	1.0	0.5	2.5	1.5	0.5
RKG Kölsch	0.5	1.5	0.5	2.0	2.5	0.5
Nachtmann Longdrink	1.5	0.0	0.0	2.0	0.0	0.0
Arcoroc Elegance	1.0	1.0	0.5	1.5	2.0	0.5
Average	1.08	1.08	0.50	2.00	1.58	0.50
Decorated Glassware	DS			DS		
Snoopy	1.0			1.0		
Teddy	0.5			1.0		
Kenia Plates	0.5			0.5		
Average	0.67			0.83		
Al-Plates	DA			DA		SU
Plate	3.0			4.0		28.0

**Table AL5b - Mass Loss**

<b>Glasses</b>	<b>50 cycles Mass Loss (mg)</b>	<b>100 cycles Mass Loss (mg)</b>
Michelangelo	3	6
Octime	0.5	4.5
Longchamp	23	48
RKG Kölsch	14	26.5
Nachtmann Longdrink	4	10
Arcoroc Elegance	5	5
<i>Sum</i>	<i>49.5</i>	<i>100</i>
<b>Decorated Glassware</b>		
Snoopy	5	11
Teddy	0	7
Kenia Plates	0	0
<i>Sum</i>	<i>5</i>	<i>18</i>
<b>Al-Plates</b>		
Plate	104.5	217

Comparative Examples 1 to 4 show that aluminium materials without protection dissolve, lose shine and cause iridescence on glassware

Addition of sodium disilicate eliminates the dissolution of aluminium materials. However, the aluminium is discoloured, turning an unpleasant brownish-black colour also the shine of the aluminium material is gone. Moreover, sodium disilicate has a negative effect on glassware: glass clouding, line corrosion and even iridescence (due to silicate rather than aluminium) occur.

Furthermore the mass loss of clear and decorated glassware is increase and the decoration protection (given by the dissolving aluminium) is no longer present.

Addition of zinc acetate reduces the mass loss of the aluminium plate (to a level  $1/20^{\text{th}}$  that as in the absence of zinc). Iridescence and glass corrosion is also improved. However, the performance on decoration protection is still poor.

Addition of bismuth citrate reduces the mass loss of the aluminium plate in a similar level to that observed with the use of zinc. However, discoloration of the aluminium increases. With bismuth the performance on decorated glass protection care is good, but the performance on glass corrosion care is weak.

**Example 1**

In this Example the base detergent formulation was used with 0.67g of zinc acetate, 0.19g bismuth citrate and 3.8g of sodium disilicate.

The results of the tests are shown in Table AL6a (Glass Corrosion) and Table AL6b (Mass Loss).

**Table AL6a - Glass Corrosion**

Glasses	50 cycles			100 Cycles				
	GC	CL	IR	GC	CL	IR		
Michelangelo	0.0	1.0	0.5	0.5	1.5	0.5		
Octime	1.0	0.5	0.0	2.5	1.5	0.5		
Longchamp	0.0	1.0	0.5	0.0	1.5	0.0		
RKG Kölsch	0.0	1.0	0.5	1.5	2.5	1.0		
Nachtmann Longdrink	1.0	0.0	0.5	0.5	0.0	0.5		
Arcoroc Elegance	0.5	1.0	0.5	1.5	1.0	1.0		
Average	0.42	0.75	0.42	1.08	1.33	0.58		
Decorated Glassware	DS		IR		DS		IR	
Snoopy	0.0				0.5			
Teddy	0.5				0.5			
Kenia Plates	0.0		0.0		1.0		0.0	
Average	0.17				0.67			
Al-Plates	DA				DA		SU	
Plate	0.5				1.0		124.83	

**Table AL6b - Mass Loss**

<b>Glasses</b>	<b>50 cycles Mass Loss (mg)</b>	<b>100 cycles Mass Loss (mg)</b>
Michelangelo	2	4
Octime	0	0
Longchamp	1	0
RKG Kölsch	5	5
Nachtmann Longdrink	3	2
Arcoroc Elegance	1	2
<i>Sum</i>	<i>12</i>	<i>13</i>
<b>Decorated Glassware</b>		
Snoopy	2	2
Teddy	0	0
Kenia Plates	0	0
<i>Sum</i>	<i>2</i>	<i>2</i>
<b>Al-Plates</b>		
Plate	16	16

The results of Example 1 show that the presence of a combination of zinc, bismuth and disilicate gives good protection to aluminium such that the corrosion is low and the aluminium keeps its shine. Additionally this combination minimises detrimental effects on glassware: iridescence, glass corrosion on plain and decorated glassware is all vastly reduced.

CLAIMS

1. A composition comprising zinc and bismuth for use in the protection of glassware in an automatic dishwashing process from detrimental effects caused by exposure of the glassware to aluminium.
2. A composition according to claim 1, wherein the ratio of zinc to bismuth in the composition is from 1:100 to 100:1 (based on mass of the metals).
3. A composition according to claim 2, wherein the ratio of zinc to bismuth in the composition (by mass) is from 1:10 to 10:1, more preferably from 1:5 to 5:1 and most preferably about 1:1.
4. A composition according to claim 1,2 or 3, wherein the zinc and / or bismuth are in metallic form.
5. A composition according to claim 4, wherein the metallic form is an alloy of zinc and bismuth.
6. A composition according to claim 1,2 or 3, wherein the zinc and / or bismuth are present as a salt or compound.
7. A composition according to claim 6, wherein the salt / compound is a nitrate, oxide, sulphate, phosphate, halide, carbonate or carboxylate salt.
8. A composition according to any one of claims 1 to 7, wherein the composition comprises a detergent formulation.

9. A composition according to claim 8, wherein the bismuth and zinc comprise from 0.002wt% to 6wt% (based on the weight of both metals) of the detergent formulation.

10. A composition according to claim 9, wherein the bismuth and zinc comprise from 0.01 to 3wt% and most preferably from 0.02 to 1.3wt% (e.g. 0.4wt%) of the detergent formulation.

11. A composition according to any one of claims 1 to 7, wherein the composition comprises a rinse aid formulation.

12. A composition according to claim 11, wherein the bismuth and zinc comprise from 0.03wt% to 30wt%, more preferable 0.15 to 15 % and most preferable 0.3 to 7 % (based on the weight of both metals) of the rinse aid formulation

13. A composition according to any one of claims 1 to 7, wherein the composition comprises a soluble ceramic / glass formulation.

14. The use of a composition comprising zinc and bismuth for the protection of glassware in an automatic dishwashing process from detrimental effects caused by exposure of the glassware to aluminium.

15. The use according to claim 14, wherein the amount of zinc and bismuth provided to a dishwasher cycle is from 1 to 1000mg.

16. The use according to claim 15, wherein the amount of zinc and bismuth provided to a dishwasher cycle is from 5 to 500mg.

17. The use according to claim 16, wherein 5 to 100 mg zinc and 5 to 100 mg bismuth is provided to a dishwasher cycle.

18. A composition comprising zinc, bismuth and aluminium for use in the prevention of glassware corrosion in an automatic dishwasher.

19. A composition containing zinc, bismuth and silicate for use in the prevention of aluminium corrosion in an automatic dishwasher.

20. A composition containing zinc, bismuth and silicate for use in the prevention of aluminium corrosion and glassware corrosion in an automatic dishwasher.



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB2004/004410

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C11D3/00 C11D3/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	DATABASE WPI Section Ch, Week 200143 Derwent Publications Ltd., London, GB; Class E12, AN 2001-406415 XP002316822 & RU 2 167 176 C2 (ISKRA RES PRODN ASSOC STOCK CO) 20 May 2001 (2001-05-20) abstract	1,6,7
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Richards, M

## INTERNATIONAL SEARCH REPORT

International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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International Application No

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